

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :

Stephane BERTAUX, et al.

Serial No. : New

Filed : February 2, 2004

For : PEARLESCENT PIGMENTS BASED ON SELECTIVELY ABSORBING  
LAYERS OF CHALCOGENIDE, OXYCHALCOGENIDE AND MIXED CHALCOGENIDES

22141 U.S. PTO  
10/768190



**SUBMISSION OF PRIORITY DOCUMENT(S)**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

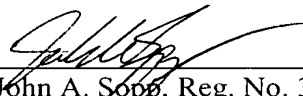
Submitted herewith is a certified copy of each of the below-identified document(s),  
benefit of priority of each of which is claimed under 35 U.S.C. § 119:

COUNTRY	APPLICATION NO.	FILING DATE
EP	03002302.2	February 3, 2003

Acknowledgment of the receipt of the above document(s) is requested.

No fee is believed to be due in association with this filing, however, the Commissioner is  
hereby authorized to charge fees under 37 C.F.R. §§ 1.16 and 1.17 which may be required to  
facilitate this filing, or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

  
\_\_\_\_\_  
John A. Sopp, Reg. No. 33,103  
Attorney/Agent for Applicants

MILLEN, WHITE, ZELANO  
& BRANIGAN, P.C.  
Arlington Courthouse Plaza I  
2200 Clarendon Blvd. Suite 1400  
Arlington, Virginia 22201  
Telephone: (703) 243-6333  
Facsimile: (703) 243-6410

Attorney Docket No.: MERCK-2826

Date: February 2, 2004

THIS PAGE BLANK (USPTO)



**Eur päisches  
Patentamt**

**European  
Patent Office**

**Office eur péen  
des brevets**

**Bescheinigung**

**Certificate**

**Attestation**

Die angehefteten Unterla-  
gen stimmen mit der  
ursprünglich eingereichten  
Fassung der auf dem näch-  
sten Blatt bezeichneten  
europäischen Patentanmel-  
dung überein.

The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

03002302.2

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**





Anmeldung Nr:  
Application no.: 03002302.2  
Demande no:

Anmeldetag:  
Date of filing: 03.02.03  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

MERCK PATENT GmbH  
Frankfurter Strasse 250  
64293 Darmstadt  
ALLEMAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se referer à la description.)

Pearlescent pigments based on selectively absorbing layers of chalcogenide,  
oxychalcogenide and mixed chalcogenides

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

C09C/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL  
PT SE SI SK TR LI

THIS PAGE BLANK (USPTO)

I 01/214 KD

**Merck Patent Gesellschaft  
mit beschränkter Haftung  
64271 Darmstadt**

**Pearlescent pigments based on selectively  
absorbing layers of chalcogenide, oxychalcogenide  
and mixed chalcogenides**

- 1 -

**Pearl scent pigments based on selectively absorbing layers of chalcogenide, oxychalcogenide and mixed chalcogenides**

5 The present invention relates to novel pearlescent pigments based on substrates comprising at least one selectively light absorbing layer which consists of a chalcogenide and/or oxychalcogenide, preferably sulfides or oxysulfides excluding rare earth and yttrium sulfides and rare earth and yttrium oxysulfides. The coatings can be directly prepared by the precipitation of chalcogenides in liquid suspension onto the substrates.

10 Preferably, metal oxides or mixed metal oxides are coated onto the substrate; the resulting precursor is transferred into a furnace and calcined under a sulfurizing gas flow to convert the oxides into oxysulfides and/or sulfides depending on the reaction parameters. The conversion to sulfides and/or oxysulfides is preferably carried out in a fluidized bed reactor. Angle-

15 dependent optical pigments are thus produced, which are especially useful in paints, powder coatings, paper coatings, plastics, cosmetics, inks and security-enhancing features as well as in decorative applications for foods and drugs.

20 Absorption pigments based on chalcogenide, oxychalcogenide and mixed chalcogenides without a layered or substrate-based structure are well known. A comprehensive overview about these substances can be found in Mane, R.S. and Lokhande, C.D., "Chemical deposition method for metal chalcogenide thin films", Materials Chemistry and Physics, 65 (2000), 1-31.

25 First attempts to use the advantages of these substances for the production of more sophisticated substrate-based effect pigments are described in US-A 6,063,179. This patent describes goniochromatic luster pigments based on silicon dioxide platelets coated with a non-selectively

30 absorbing film-like layer at least partially transparent to visible light, and if desired an outer layer which consists essentially of colorless or selectively



- 2 -

absorbing metal oxide and/or comprises a phosphate, chromate and/or vanadate. The nonselectively absorbing layer can be a metal sulfide, such as iron, cobalt, nickel, chromium, molybdenum and tungsten sulfide. These layers are non-selectively absorbing light which result in primarily black or dark colored pigments.

A layer is selectively absorbing if there is a higher or lower absorption in a certain region of the electromagnetic spectrum. The result is a real color effect different from white-gray-black (Coating (2001)(4) 135; chroma according to DIN 5033 and DIN 6174).

A number of pigments based on sulfides and oxysulfides are disclosed in DE-A 19 81 03 17. Specifically platelet-shaped substrates coated with sulfides having the formula  $M_2S_3$  and oxysulfides having the formula  $M_2S_{3-x}O_x$  ( $0.05 \leq x \leq 2.5$ ) are mentioned in which M is a rare earth element or yttrium. The substrates are chosen from natural and synthetic mica,  $SiO_2$ -,  $TiO_2$ -,  $Al_2O_3$ -flakes, glass flakes, graphite,  $BiOCl$ , kaolin, talc, vermiculite, iron oxide flakes and metal flakes. These substrates may be uncoated or coated with one or more layers of oxides under the sulfide respectively oxysulfide layer. The sulfide respectively oxysulfide layers may be doped with one or more alkali ions, such as Na or K ions. The process for making these pigments comprises coating the substrates with an oxide, an oxide hydrate or an oxalate through a precipitation process. Then the pigments are dried, calcined between  $400^\circ C$  and  $800^\circ C$  and converted into sulfides respectively oxysulfides under S,  $CS_2$ ,  $H_2S$  or a compound containing S. Due to the usage of rare earth elements, these pigments and their production are high priced what limits the usability in applications.

It was therefore an object of the present invention to provide readily available pigments with a great variety of different mass-tones which combine an viewing angle dependant interference phenomenon with the absorption color, therewith extending the range of pearlescent pigments

- 3 -

based on chalcogenides/oxychalcogenides.

5 The pigments according to the present invention can surprisingly fulfill the above-mentioned object. Therefore, the present invention describes pearlescent pigments based on substrates comprising at least one selectively light absorbing layer which consists of chalcogenide and/or oxychalcogenide excluding rare earth and yttrium sulfides and rare earth and yttrium oxysulfides. Preferably the chalcogenide and/or oxychalcogenide is a metal chalcogenide and/or metal oxychalcogenide with a metal being selected from group 2 and/or 4-16 of the periodic system.

15 The chalcogenide-, oxychalcogenide- and mixed chalcogenide-containing coatings can be prepared by the precipitation of chalcogenides onto substrates in liquid suspension onto the substrates. For example, sodium sulfide and a metal chloride are simultaneously added to a suspension of platelet-shaped substrates leading to a hydrous metal sulfide coating onto said substrates. In a similar way, ammonium sulfide, ammonium polysulfide or sodium selenide or sodium telluride can be used. The resulting coated substrate, the so-called precursor, is separated from the mother liquid, dried and preferably calcined. The selenide or telluride main components and dopants can also be precipitated via decomposition or hydrolysis of organic precursors in gas phase, aqueous phase or non-aqueous main phase reactions, e.g. using  $R^1\text{-Se-R}^2$  or  $R^1\text{-Te-R}^2$  as educts with  $R^1$  respectively  $R^2 = \text{alkyl, aryl, Me}_3\text{Si}$ .

30 The preferred synthesis of the new pigments, however, is performed via a two-step process including a gas phase reaction. The first step is the synthesis of a precursor based on a substrate. The second step is a conversion process, carried out in a furnace. The pearlescent pigments according to the present invention can be produced in conventional static ovens, belt kilns or rotary kilns. However, a commercially more attractive

- 4 -

product with less agglomerates and faster reaction rates is obtained in fluidized bed reactors.

In the first step a layer of an oxide, hydroxide, mixed oxide and/or mixed hydroxide is deposited onto a substrate, thus obtaining the precursor being used in the second step. All known deposition techniques, such as aqueous precipitation processes, CVD and/or PVD processes can be used. However, preferably an aqueous precipitation process described for example in US-A 3,087,828, US-A 3,087,829, DE-A 19 59 998, DE-A 20 09 566, DE-A 22 14 545, DE-A 22 44 298, DE-A 23 13 331, DE-A 25 22 572, DE-A 31 37 808, DE-A 31 37 809, DE-A 31 51 343, DE-A 31 51 354, DE-A 31 51 355, DE-A 32 11 602, DE-A 32 35 107, WO 93/08237 and EP-A 0 763 573 is used to obtain the precursor. Halide-, carbonate-, oxalate-, chloride- or oxychloride solutions are used to precipitate oxides, hydroxides, mixed oxides and/or mixed hydroxides onto the substrates. The reaction parameters such as temperature, pH, agitation velocity and reactor geometry are optimized to yield a flat continuous layer of the insoluble oxides and/or hydroxides on the substrates. The mixed oxides and/or hydroxides are co-precipitated onto the substrates following an analogous process. Solutions of the different metal salts are mixed and then slowly added in the reactor to coat the substrate. The oxide, hydroxide, mixed oxide and/or mixed hydroxide can be doped with metal ions, silicon oxide, aluminum oxide, boron oxide, sulfur, phosphate ions and/or sulfate ions. The dopants can be used to create color effects (like rare earths, vanadium, or cobalt ions) as well as for the control of grain growth (like  $\text{SiO}_2$  or aluminum oxide) during the subsequent second step. For the latter purpose, for example, small amounts sodium silicate or soluble borates can be added to the coating solution via the metal salt or the acidic respectively caustic solutions that are used to adjust the pH. Examples of metal ions as dopant are silicon, vanadium, chromium, aluminum, cerium, neodymium, praseodymium, selenium, cobalt, nickel and/or zinc ions, preferably vanadium and/or cobalt ions.

- 5 -

Substrates that can be used in the present invention as base material on which the oxides, hydroxides, mixed oxides and/or mixed hydroxides are precipitated include platelet-shaped, spherical or needle-shaped substrates. Preferably the substrates comprise but are not limited to:

5

Platelets: Micaceous iron oxide, natural (for example as in WO 99/48634), synthetic or doped (for example as in EP-A 0 068 311) micas (muscovite, phlogopite, fluoro-phlogopite, synthetic fluorophlogopite, talc, kaolin), basic lead carbonate, platelet-shaped barium sulfate,  $\text{SiO}_2$ -,  $\text{Al}_2\text{O}_3$ -,  $\text{TiO}_2$ -, Glass-,  $\text{ZnO}$ -,  $\text{ZrO}_2$ -,  $\text{SnO}_2$ -,  $\text{BiOCl}$ -, chromium oxide-, BN-,  $\text{MgO}$ - flakes,  $\text{Si}_3\text{N}_4$ , graphite, pearlescent pigments (including those which react under the fluidized bed conditions to nitrides, oxynitrides or by reduction to suboxides etc.) (for example EP-A 9 739 066, EP-A 0 948 571, WO 99/61529, EP-A 1 028 146, EP-A 0 763 573, US-A 5,858,078, WO 98/53012, WO 97/43348, US-A 6,165,260, DE-A 15 19 116, WO 97/46624, EP-A 0 509 352), pearlescent multilayer pigments (for example EP-A 0 948 572, EP-A 0 882 099, US-A 5,958,125, US-A 6,139,613) and/or metals. Preferably, the metal is aluminum and/or titanium, most preferably passivated by inorganic treatment.

20

Spheres: coated  $\text{SiO}_2$  spheres (for example EP-A 0 803 550, EP-A 1 063 265, JP-A 11 322 324), uncoated  $\text{SiO}_2$  spheres (Ronaspheres<sup>®</sup>, all spheres described as starting materials in EP-A 0 803 550, EP-A 1 063 265, JP-A 11 322 324), micro bubbles (US-A 4,985,380), as well as needle-shaped metal oxides, preferably iron oxide.

25

The mean diameter of the substrates and hence the resulting pigments can vary between 1 and 500  $\mu\text{m}$ , preferably 5 and 50  $\mu\text{m}$ . Pronounced interference effects can be obtained in the case of platelet-shaped substrates with a preferred mean diameter between 10 and 150  $\mu\text{m}$ . Such substrates are commercially available or can be obtained by known processes.

30

- 6 -

5 The chalcogenide and/or oxychalcogenide layer can be coated directly onto the substrate as described above. In the same way nitride respectively oxynitride layer coated substrates can be used as substrates to precipitate the optical layers as described above.

10 In the second step the for the production of pigments according to the present invention the oxides, hydroxides, mixed oxides and/or mixed hydroxides obtained in the above described first step are converted into chalcogenides and/or oxychalcogenides. This can be achieved by calcination of the precursor obtained in the first step in conventional static ovens, belt kilns or rotary kilns. However, a better product with less agglomerates and faster reaction rates is obtained in fluidized bed reactors. This process can be performed batchwise or continuously. The conversion is carried out with a reactive gas, which may consist of  $H_2S$ ,  $CS_2$ , sulfur and/or a mixture of these. Additionally an inert gas such as Ar or  $N_2$ , preferably  $N_2$  may be present during the conversion. The gas composition may vary from >0 to 100 vol-%, preferably from 20 to 80 vol-% of reaction gas in inert gas.

20 The temperature is maintained at a fluidized bed temperature of about 700-1250°C, preferably 800°C to 1100°C. The conversion between oxides, hydroxides, mixed oxides as well as mixed hydroxides and chalcogenides and/or oxychalcogenides is carried out depending on the different parameters, such as gas flow rates, reaction time or temperature profiles. The longer the reaction time the higher the chalcogenide-to-oxychalcogenide ratio. Consequently the reaction time determines obtained structure of the compound. The color and the color strength of the pearlescent pigments according to the present invention is associated to a determined structure that is why the reaction time has to be well controlled. In addition for the same reason the temperature control is necessary. The control and optimization of the process parameters can be performed by any

- 7 -

person skilled in the art.

In order to maintain the almost ideal conditions prevalent in an homogeneous fluid bed in comitercurrent/cocurrent contacting special devices are used. Instabilities like formation of channels or of bubbles in the bed are instantly destroyed by vibrations or agitating facilities.

If the reaction with the reaction gas is not carried out to full completeness, mixtures of phases can be obtained including gradient of phase concentration through the layer thickness. These incompletely reacted products can be advantageous with respect to a desired color shade.

The thickness of the chalcogenide and/or oxychalcogenide layers can vary between 5 and 500 nm, yielding slight shades and flat angle color effect at low thickness and very pronounced hiding at high thickness. For the optimal interference effect, the preferred thickness is 50-350 nm, especially preferred 80-200 nm.

The interference color is determined by the optical thickness, which is the geometrical thickness of the layer multiplied by the refractive index (Pfaff, G.; Reynders, P. "Angle-dependent optical effects deriving from submicron structures of films and pigments", Chemical Review, 99 (1999), p.1963-1981). The latter is a strong function of the chosen material but is in general not known for the rather new materials mentioned in this invention. The mass tone of the absorbing pigments is as well a function of the layer thickness. Therefore, the desired color effect is empirically optimized by adjustment of the amount of precursor, by this means controlling the precursor layer thickness, and regulation of the conversion reaction with the reactive gases.

Preferably, the selectively light absorbing layer of chalcogenides and/or oxychalcogenides may consist of:

- 8 -

Sulfides:

## 1. Sulfides containing one metal:

- $A_xS_y$  with  $A = \text{Zr, Fe, Zn, Mn, Co, Ni, Cu, In, Sn, Pb, Ag, Bi, Sb, As, Cr, Mo, W, Rb, Ti}$

$x > 0, y > 0$

such as  $\text{ZnS, FeS}_2, \text{Fe}_3\text{S}_4, \text{MoS}_2$

- $A_xS_y$  doped with  $\text{Ag, Al, Au, Cu, Eu, Sm}$  or a mixture of these cations, such as  $\text{ZnS:Ag, ZnS:Al, ZnS:Au, ZnS:Cu, ZnS:Cu or Al, ZnS:Cu or Al or Au, SrS:Eu or Sm, SrS:Ce or Sm, SrS:Cu}$  and with  $x > 0, y > 0$

- $A_xS_y$  doped with  $\text{Eu}_m, \text{Tr}_n$  and  $\text{O}_p\text{X}_q$

with  $A = \text{alkaline earth metal ion,}$

$\text{Tr} = \text{one or more trivalent rare earth metal ions,}$

$X = \text{halide,}$

$0.01 < m < 0.5, 0.01 < p < 2, 0.01 < q < 0.5$  (values in atomic percent), or  $m, n,$

$p, q$  are integers,

such as  $\text{SrS:Eu:Er:OCl, SrS:Eu}_{0.1}:\text{Er}_{0.1}:\text{Dy}_{0.1}:\text{OCl}$

## 2. Sulfides containing two or more metals:

$\text{CuInS}_2, \text{CuBiS}_2, \text{CuFeS}_2, \text{Rb}_4\text{Ta}_2\text{S}_{11}, \text{CuPrS}_2, \text{Nd}_2\text{TeS}_2$

$\text{EuCe}_2\text{S}_4, \text{CaLa}_2\text{S}_4, \text{Cu}_5\text{FeS}_4, \text{CuCr}_2\text{S}_4,$

$\text{Pb}_x\text{Ca}_{1-x}\text{La}_2\text{S}_4,$

such as  $\text{Pb}_{0.1}\text{Ca}_{0.9}\text{La}_2\text{S}_4, \text{PbCeS}_4$

- $\text{Na}_4\text{SiS}_{10}, \text{Ce}_3\text{Si}_2\text{I}_8, \text{ZnSeS}, \text{ZnSe}_{0.53}\text{S}_{0.47}, \text{TiSeS}, \text{K}_4\text{Nb}_2\text{S}_{10}, \text{K}_6\text{Nb}_4\text{S}_{25}$

- $\text{Zn}_{3-3x}\text{In}_{2y}\text{Ga}_{2x-2xy}\text{S}_3$

- 9 -

with  $0.2 < x < 0.97$ ,  $0.1 < y < 1$ -  $\text{ZnIn}_2\text{S}_4$ ,  $\text{Zn}_2\text{In}_2\text{S}_5$ -  $\text{A}_8\text{Nb}_4\text{S}_{22}$ with  $\text{A} = \text{Rb}, \text{Cs}$ 

5

 $\text{CuGa}_5\text{S}_8$ ,  $\text{CuIn}_5\text{S}_8$ -  $\text{AgGa}_x\text{In}_{5-x}\text{S}_8$  with  $0 \leq x \leq 3$ ,such as  $\text{AgGa}_3\text{In}_2\text{S}_8$ ,  $\text{AgGa}_5\text{S}_8$ ,  $\text{AgIn}_5\text{S}_8$ ,  $\text{AgGa}_4\text{InS}_8$ 

10

-  $\text{Rb}_4\text{Ti}_3\text{S}_{14}$ ,  $\text{Cs}_4\text{Zr}_3\text{S}_{14}$ ,  $\text{K}_4\text{Ti}_3\text{S}_{14}$ ,  $\text{Ti}_2\text{TiS}_4$ ,  $\text{Cs}_2\text{TiS}_3$ ,  $\text{K}_2\text{TiS}_3$ ,  $\text{Na}_2\text{ZrS}_3$ ,  
 $\text{Ba}_3\text{Zr}_2\text{S}_7$ ,  $\text{Cu}_2\text{HfS}_3$ ,  $\text{Cu}_4\text{TiS}_4$ ,  $\text{Ag}_4\text{Hf}_3\text{S}_8$ ,  $\text{Ag}_2\text{HfS}_3$ -  $\text{KLnMS}_4$ 

15

with  $\text{Ln} = \text{rare earth or Y}$ , $\text{M} = \text{Si, Ge}$ ,such as  $\text{KCeSiS}_4$ ,  $\text{KLaGeS}_4$ -  $\text{Ca}_{(1-x)}\text{Yb}_{(2/3 x)}\text{Defect}_{(1/3 x)}\text{S}$  with  $0 \leq x \leq 1$ 

20

Oxysulfides:-  $\text{ZrOS}$ ,  $\text{Rb}_4\text{Nb}_2\text{OS}_{10}$ 

25

 $\text{Na-Sr-Cu-M-O-S}$ with  $\text{M} = \text{Zn, Ga, In}$ preferably  $\text{Sr}_{2-x}\text{Na}_x\text{Cu}_2\text{ZnO}_2\text{S}_2$ ,  $\text{Sr}_{2-x}\text{Na}_x\text{CuGaO}_3\text{S}$  with  $x > 0$ , $\text{Sr}_2\text{Cu}_2\text{ZnO}_2\text{S}_2$ ,  $\text{Sr}_2\text{CuGaO}_3\text{S}$ ,  $\text{Sr}_2\text{CuInO}_3\text{S}$ 

30

Selenides: $\text{A}_x\text{Se}_y$



- 10 -

with A = Cd, Zn, Bi, Sb, Ni, Tl, Pb, Cu, Mo, Sn, Co, with  $x > 0$ ,  $y > 0$   
such as ZnS, Bi<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, NiSe, TlS, PbSe, CuSe, MoSe<sub>2</sub>, SnS, CoSe

5 - Cd<sub>x</sub>Pb<sub>y</sub>Se with  $x > 0$ ,  $y > 0$

- CuInSe<sub>2</sub>

- Cd<sub>1-x</sub>Zn<sub>x</sub>Se ( $0 \leq x \leq 0.9$ )

10

- Cd<sub>1-x</sub>Fe<sub>x</sub>Se ( $0 \leq x \leq 0.9$ )

Sulfoselenides:

15 CdS<sub>x</sub>Se<sub>y</sub>, ZnS<sub>x</sub>Se<sub>y</sub> with  $x > 0$ ,  $y > 0$

20 The new pearlescent pigments can be used as substrate to precipitate further optical layers. If desired, the pearlescent pigments according to the present invention can be further coated with one or more layers of metal oxides and/or semitransparent metal layers on top of the selectively light absorbing layer. The metal oxide can be selected from any metal oxide, preferably from titanium oxide, iron oxide, aluminum oxide, silicon oxide, zirconium oxide, chromium oxide and/or zinc oxide, most preferably from

25 titanium oxide, iron oxide and/or mixtures thereof. The metal of the semitransparent metal layer can be selected from chromium, molybdenum, aluminum, silver, platinum, nickel and/or copper, preferably from aluminum, molybdenum and/or chromium.

30 Furthermore, the resulting pigments can be coated with inorganic and/or organic compounds to increase their weather stability respectively their photostability. Usful methods are for instance described in US-A

- 11 -

4,134,776, EP-A 0 649 886, WO 97/29059 and references cited therein.

The advantage of this invention is the combination of a great variety of mass-tones of the chalcogenides and derived compounds with an angle dependent interference color that is adjusted by the layer thickness of the chalcogenide/oxychalcogenide-containing layer. The applications of these new pigments are numerous, such as paints, powder coatings, paper coatings, plastics, cosmetics, inks and security-enhancing features as well as in decorative applications for foods and drugs due to the use of mainly nontoxic materials.

To create new color effects in all applications, the pearlescent pigments according to the present invention can be employed in admixture with filler pigments or transparent and hiding white, colored and black organic and inorganic pigments and also with conventional transparent, colored and black luster pigments based on metal oxide coated mica,  $\text{TiO}_2$  flakes,  $\text{SiO}_2$  flakes or  $\text{Al}_2\text{O}_3$  flakes and coated or uncoated metal pigments,  $\text{BiOCl}$  pigments, platelet-shaped iron oxides or graphite flakes. The inventive pigments can be further coated with organic or inorganic layers to yield combination pigments.

Some layers of the pigments described in this invention have fluorescent, photoluminescent or electroluminescent properties itself, e.g. doped  $\text{ZnS}$  layers. If such a time-delayed color effect is desired, for example in the field of security, optical, projections screen, safety or similar applications, and the inherent property of the invented pigments is not strong enough, physical mixtures of the invented pigments with conventional inorganic or organic fluorescent respectively luminescent pigments can be used.

The pigments and their production process according to the present invention is more illustratively demonstrated but not limited by means of the following examples.

- 12 -

**Examples:****Example 1:**

5 100 g of muscovite mica (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended  
in 2 liters of fully deionised water. The suspension is heated to 75°C. 467  
ml of a  $\text{FeCl}_3$ -solution is diluted to 1000 ml with water and is slowly added  
to the reactor. The pH of the solution is kept at pH 3.1 by addition of 15%  
aqueous sodium hydroxide solution. The preparation is filtered off, washed  
10 with completely deionised water, dried at 110°C for 12 hours and calcined  
at 800°C for 30 minutes. As a result, 70 g of  $\text{Fe}_2\text{O}_3$  are precipitated onto  
100 g of mica. This pigment is then put into a fluidized bed reactor,  
calcined under  $\text{H}_2\text{S}$  at 900°C during 12 hours. A yellow to golden  
 $\text{FeS}_2$ /mica pigment is obtained.

15

**Example 2:**

20 100 g Iriodin® 504 ( $\text{Fe}_2\text{O}_3$ /mica, Merck KGaA) are suspended in 2 liters of  
fully deionised water. The suspension is heated to 75°C. A  $\text{ZrOCl}_2$  solution  
(72.3 g diluted in 600ml water) is slowly added to the reactor. The solution  
is kept at pH 3 by simultaneous addition of 15% aqueous sodium hydroxide  
solution. The preparation is filtered off, washed with completely deionised  
water and dried at 110°C for 12 hours. As a result, 50 g of  $\text{ZrO}_2$  are  
precipitated onto 100 g of Iriodin® 504. The pigment is then put into a  
25 fluidized bed reactor. The precursor is fluidized with  $\text{N}_2$  to 750-850°C and  
then is treated with  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a reddish golden  
color (mixed iron sulfide) and a yellow shade (zirconium oxysulfide) is  
obtained.

30

- 13 -

**Example 3:**

100 g  $\text{SiO}_2$  flakes (Merck KGaA, diameter 10-50  $\mu\text{m}$ ) are suspended in 2  
liters of fully deionised water. The suspension is heated to 75°C. A  $\text{ZrOCl}_2$   
5 solution (72.3 g diluted in 600 ml water) is slowly added into the reactor.  
The solution is kept at pH 3 by addition of 15% aqueous sodium hydroxide  
solution. The preparation is filtered off, washed with completely deionised  
water, dried at 110°C for 12 hours. As a result, 50 g of hydrous  $\text{ZrO}_2$  are  
precipitated onto 100 g of  $\text{SiO}_2$  flakes. The pigment is then put into a  
10 fluidized bed reactor. The precursor is fluidized with  $\text{N}_2$  to 750-850°C and  
then is converted with  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a yellow color  
(zirconium oxysulfide) is obtained.

**Example 4:**

50 g of  $\text{ZrO}_2\text{:VCl}_3$  (10:1 wt.-ratio) are precipitated onto 100 g of  $\text{SiO}_2$ -flakes  
(Merck KGaA, diameter 10-50  $\mu\text{m}$ ) using a  $\text{ZrOCl}_2$ -solution (72.3 g of  
 $\text{ZrOCl}_2$  solution containing 7.2 g of  $\text{VCl}_3$  diluted into 600 ml of water) as  
20 described in the example 3. The dried pigment is then put into the fluidized  
bed, calcined at 800°C under  $\text{H}_2\text{S}$  for 360 minutes. A pigment with a blue  
color (vanadium-doped zirconium oxysulfide) was obtained.

**Example 5:**

A metallized zirconium oxysulfide pigment is produced by thermally  
decomposing chromium hexacarbonyl in the presence of heated zirconium  
oxysulfide coated onto  $\text{SiO}_2$  flakes as described in the example 3. This  
30 pigment is fluidized with nitrogen to achieve and maintain a non-bubbling  
fluidized bed and an oxygen free atmosphere. Then the reactor is heated to  
400-450°C and kept under this condition throughout the following coating

- 14 -

process. A stream of nitrogen loaded with chromium hexacarbonyl is prepared by passing nitrogen through a flask containing chromium hexacarbonyl, which is kept at 80°C, and introduced subsequently into the reactor. The vaporized compound is passed into the tube for about 90 minutes. About 5 nm of chromium is deposited on the zirconium oxysulfide pigment based onto SiO<sub>2</sub> flakes, forming a semitransparent layer. The organic by-product of the decomposition reaction is separated from the pigment into a scrubber.

#### Example 6:

100 g of muscovite mica (Merck KGaA, diameter 10-50 µm) are suspended in 2 liters of fully deionised water. The suspension is heated to 75°C. A ZnCl<sub>2</sub> solution (84 g) is mixed with a CuCl<sub>2</sub> solution (10 g) and the mixture is slowly added to the reactor. The solution is kept at pH 3 by addition of 15% aqueous sodium hydroxide solution. The preparation is filtered off, washed with completely deionised water, dried at 110°C for 12 hours and then calcined at 850°C for 30 minutes. As a result, 50 g of ZnO:Cu are precipitated onto 100 g of mica. This pigment is then put into a fluidized bed reactor, calcined under H<sub>2</sub>S at 1000°C during 12 hours. A blue ZnS:Cu/mica pigment is obtained.

#### Example 7:

100 g of silica flakes (Merck KGaA, diameter 10-50 µm) are suspended in 2 liters of fully deionised water. The suspension is heated to 65°C. A solution of 83 g ZnSO<sub>4</sub> (120 g/l Zn) containing 0.01 mol% CuSO<sub>4</sub> is slowly added simultaneously with a solution of 40 g Na<sub>2</sub>S (60 g/l Na<sub>2</sub>S) into the reactor. The solution is kept at pH 3.5 by addition of dilute hydrochloric acid solution. The pH is increased to 7 and another small quantity of Na<sub>2</sub>S is

- 15 -

added in the reactor. The preparation is filtered off, washed with completely deionised water, dried at 130°C for 12 hours and then calcined at 900°C for 120 minutes. As a result, a white zinc sulfide containing pigment is obtained showing luminescence.

5

Example 8:

100 g of muscovite mica flakes (Merck KGaA, diameter 10-50 µm) are suspended in 2 liters of fully deionised water. The suspension is heated to 75°C. A solution of 67.2 g SbCl<sub>3</sub> diluted with 200 g 32% HCl is slowly added simultaneously with a solution of 34.54 g Na<sub>2</sub>S into the reactor. The solution is kept at pH 3.5 by addition of dilute hydrochloric acid solution. The preparation is filtered off, washed with completely deionised water, dried at 110°C for 12 hours and then calcined at 450°C for 60 minutes. As a result, an orange antimony(III) sulfide containing pigment is obtained.

15

Example 9:

20

100 g of silica flakes (Merck KGaA, diameter 10-50 µm) are suspended in 2 liters of fully deionised water. The suspension is heated to 65°C. A solution of 67 g ZnSO<sub>4</sub> (120 g/l Zn) containing 0.01 mol% CuSO<sub>4</sub> is slowly added simultaneously with a solution of 16 g Na<sub>2</sub>S (60 g/l Na<sub>2</sub>S) and 26 g Na<sub>2</sub>Se into the reactor. The solution is kept at pH 3.5 by addition of dilute hydrochloric acid solution. The pH is increased to 7 and another 0.5 g Na<sub>2</sub>S is added in the reactor. The preparation is filtered off, washed with completely deionised water, dried at 130°C for 12 hours and then calcined at 600°C for 120 minutes. As a result, a white zinc sulfoselenide containing pigment is obtained.

25

30

- 16 -

### Claims

1. Pearlescent pigments based on substrates comprising at least one selectively light absorbing layer which consists of a chalcogenide and/or oxychalcogenide excluding rare earth and yttrium sulfides and rare earth and yttrium oxysulfides.  
5
2. Pearlescent pigments according to claim 1, characterized in that the chalcogenide and/or oxychalcogenide is a metal chalcogenide and/or metal oxychalcogenide with a metal being selected from group 2 and/or 4-16 of the periodic system.  
10
3. Pearlescent pigments according to claim 1 or 2, wherein the substrate is platelet-shaped, spherical or needle-shaped.
- 15 4. Pearlescent pigments according to claim 3, wherein the substrate is platelet-shaped and is of mica,  $\text{SiO}_2$ , aluminum oxide, glass, micaceous iron oxide, oxidized graphite, aluminum oxide-coated graphite, basic lead carbonate, barium sulfate, chromium oxide, BN, MgO,  $\text{Si}_3\text{N}_4$ , metal, pearlescent pigments or pearlescent multilayer pigments, or of coated or uncoated  $\text{SiO}_2$ -spheres or needle-shaped iron oxides.  
20
5. Pearlescent pigments according to claim 3, characterized in that the metal is aluminum or titanium, passivated by inorganic treatment.  
25
6. Pearlescent pigments according to any of claims 1 to 5, characterized in that the selectively light absorbing layer is a sulfide, oxysulfide, selenide and/or sulfoselenide.
- 30 7. Pearlescent pigments according to one of claims 1 to 6, characterized in that the pigments are further coated on top of the selectively light

- 17 -

absorbing layer with one or more layers of metal oxides and/or semitransparent metal layers.

- 5           8.    Pearlescent pigments according to claim 7, characterized in that the metal oxide is selected from  $\text{TiO}_2$  and/or iron oxide and the metal is selected from Al, Mo and/or Cr.
- 10        9.    Process for the preparation of a pigment according to claim 1 comprising precipitating a layer of an oxide, hydroxide, mixed oxide and/or mixed hydroxide onto a substrate and then converting the oxide, hydroxide, mixed oxide and/or mixed hydroxide into a chalcogenide and/or oxychalcogenide.
- 15        10.   Process according to claim 9, characterized in that the substrate is platelet-shaped and is of mica,  $\text{SiO}_2$ , aluminum oxide, glass, micaceous iron oxide, oxidized graphite, aluminum oxide-coated graphite, basic lead carbonate, barium sulfate, chromium oxide, BN,  $\text{MgO}$ ,  $\text{Si}_3\text{N}_4$ , metal, pearlescent pigments or pearlescent multilayer pigments, or of coated or uncoated  $\text{SiO}_2$ -spheres or needle-shaped iron oxides.
- 20        11.   Process according to claim 9, characterized in that the oxide, hydroxide, mixed oxide and/or mixed hydroxide is doped with metal ions, silicon oxide, aluminum oxide, boron oxide, sulfur, phosphate ions and/or sulfate ions.
- 25        12.   Process according to claim 11, characterized in that the metals are selected from silicon, vanadium, chromium, aluminum, cerium, neodymium, praseodymium, cobalt, nickel and/or zinc.
- 30        13.   Process for the preparation of a pigment according to claim 1 comprising precipitating a layer of a chalcogenide onto a substrate by



- 18 -

adding a chalcogenide solution and a metal salt or metal complex solution to a suspension of the substrate and then drying the precipitated layer.

- 5        14. Use of a pigment according to one of claims 1 to 8 in paints, powder coatings, paper coatings, plastics, cosmetics, inks, decorative applications for foods and drugs and security-enhancing features.
- 10       15. Use of a pigment according to any of claims 1 to 8 as phosphorescent, fluorescent or luminescent materials in security, optical or projection screen applications.

15

20

25

30

- 19 -

**Summary of the Invention**

The present invention relates to novel pearlescent pigments based on substrates comprising at least one selectively light absorbing layer which consists of a chalcogenide and/or oxychalcogenide, preferably sulfides or oxysulfides. The coatings can be directly prepared by the precipitation of chalcogenides in liquid suspension onto the substrates. Preferably, metal oxides or mixed metal oxides are coated onto the substrate; the resulting precursor is transferred into a furnace and calcined under a sulfurizing gas flow to convert the oxides into oxysulfides and/or sulfides depending on the reaction parameters. The conversion to sulfides and/or oxysulfides is preferably carried out in a fluidized bed reactor. Angle-dependent optical pigments are thus produced, which are especially useful in paints, powder coatings, paper coatings, plastics, cosmetics, inks and security-enhancing features as well as ion decorative applications for foods and drugs.